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(54) Title: REFRIGERANT BLENDS CONTAINING 1,1,1,2,3,3,3-HEPTAFLUOROPROPANE (57) Abstract Refrigerant compositions are disclosed which comprise a mixture of 1,1,1,2,3,3,3-heptafluoropropane, and one or more compounds selected from the group consisting of methane, ethane, propane, butane, difluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,2-trifluoroethane, dimethyl ether, isobutane, 2-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane and cyclopropane. The 1,1,1,2,3,3,3-heptafluoropropane preferably comprises between about 10 and about 90 weight percent of the composition, and a lubricant may also be present. Methods of cooling and heating by use of such compositions are also disclosed.		

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**REFRIGERANT BLENDS CONTAINING
1,1,1,2,3,3,3-HEPTAFLUOROPROPANE**

BACKGROUND OF THE INVENTION

Field of the Invention:

5 The present invention relates to refrigeration and refrigerants, more particularly to the use of refrigerants containing 1,1,1,2,3,3,3-heptafluoropropane. The mixtures of the present invention have essentially no effect on stratospheric ozone and are useful as refrigerants for
10 heating and cooling applications.

Description of the Prior Art:

 The arts of refrigeration and heating are well known, and their related technology has seen widespread commercial use. Refrigeration or heating can be described as the utilization
15 of a physical change in a substance to produce a cooling or heating effect. For example, a method for producing refrigeration comprises condensing a suitable agent, and thereafter evaporating the agent in the vicinity of the body to be cooled. Conversely, such agents may be utilized for
20 producing heat by condensing the agent in the vicinity of the body to be heated, and thereafter evaporating the agent.

 A number of chlorofluorocarbons (CFCs) have gained widespread use in refrigeration and heating applications owing to their unique combination of physical and chemical
25 properties. For example, dichlorodifluoromethane (R12) is

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employed extensively in mobile (automobile) air conditioning and chlorodifluoromethane (R22) is commonly employed in residential heat pumps. However, due to their implication in the destruction of stratospheric ozone, the production and
5 use of CFCs is currently being severely restricted, and it is expected that the use of these agents will be completely banned in the near future. This will require the replacement of these agents by refrigerants containing neither chlorine nor bromine, and which have no effect on stratospheric ozone.
10 One such zero ozone depleting compound which has been proposed is 1,1-difluoroethane (refrigerant R152a), which has been shown to provide 4 to 10% increases in efficiency compared to dichlorodifluoromethane (R12), as discussed by Kuijpers, et al., in "CFCs: Time of Transition," ASHRAE,
15 Atlanta, Ga., 1989, p. 175. A major drawback of this compound, however, is its high flammability.

Additional compounds which have been proposed include the halocarbons difluoromethane (R32), 1,1,1-trifluoroethane (R143a), 1,1,2-trifluoroethane (R143), and 1,1-difluoroethane
20 (R152a). However, the flammability of these compounds, and additionally the high vapor pressures of R32 and R143a, have precluded the practical use of these compounds. Hydrocarbons such as methane (R50), ethane (R170), propane (R290), and butane (R600) have also been employed as refrigerants, but
25 their uses are severely restricted due to their high flammability.

The art has been continually seeking new fluorocarbon based mixtures which offer alternatives for refrigeration and heat pump applications, and which are efficient, nontoxic,
30 non-ozone depleting and nonflammable.

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SUMMARY OF THE INVENTION:

Briefly describing one aspect of the present invention, there are provided refrigerant compositions including 1,1,1,2,3,3,3-heptafluoropropane and one or more of methane, 5 ethane, propane, butane, difluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane and 1,1,2-trifluoroethane, dimethyl ether, isobutane, 2-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane and cyclopropane. These 10 compositions display good refrigerant properties, and are nontoxic, non-ozone depleting and nonflammable. Computer-based models have substantiated that these compounds have no effect on stratospheric ozone, i.e., their ozone depletion potential (ODP) is zero. Methods for producing 15 cooling and heating by use of the foregoing compositions are also provided.

It is accordingly an object of this invention to provide novel compositions based on 1,1,1,2,3,3,3-heptafluoropropane which are novel, environmentally acceptable refrigerants 20 which are useful in cooling and heating applications. Another object of the invention is to provide such refrigerant blends which are nontoxic, chemically stable, and present no adverse threat to stratospheric ozone. Other objects of the invention will become apparent from the 25 following description.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the preferred embodiment of the invention and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, modifications and further applications of the principles of the invention being contemplated as would normally occur to one skilled in the art to which the invention relates.

In accordance with the invention, novel refrigerant mixtures have been discovered comprising 1,1,1,2,3,3,3-heptafluoropropane (R227ea) in admixture with a second compound selected from the group consisting of methane (R50), ethane (R170), difluoromethane (R32), 1,1,1-trifluoroethane (R143a), 1,1,2-trifluoroethane (R143), 1,1-difluoroethane (R152a), propane (R290), butane (R600), dimethyl ether, isobutane (R600a), 2-chloro-1,1,1,2-tetrafluoroethane (R124), pentafluoroethane (R125), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2-tetrafluoroethane (R134a) and cyclopropane (RC270). The compositions comprise from about 10 to about 90 weight percent 1,1,1,2,3,3,3-heptafluoropropane and from about 90 to about 10 weight percent of the second compound. It is a feature of one aspect of the present invention that the 1,1,1,2,3,3,3-heptafluoropropane in combination with a second refrigerant which is itself a flammable compound yields a non-flammable mixture having desirable refrigerant properties. The refrigerant mixtures of the present invention are useful in compression cycle applications including air conditioner and heat pump systems, and are useful for producing both cooling and heating.

In a preferred embodiment of the invention, the refrigerant mixtures comprise from about 20 to 80 weight

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percent 1,1,1,2,3,3,3-heptafluoropropane, and from about 80 to 20 weight percent of a second compound selected from the group consisting of difluoromethane (R32), 1,1,1-trifluoroethane (R143a), 1,1,2-trifluoroethane (R143), 1,1-difluoroethane (R152a), propane (R290), butane (R600), dimethyl ether, isobutane, methane (R50), ethane (R170), 2-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane and cyclopropane. Mixtures containing larger percentages of 1,1,1,2,3,3,3-heptafluoropropane exhibit wider ranges of nonflammability, whereas those mixtures rich in the second component offer advantages in increased refrigerant volumetric capacity. As a result, the mixture compositions can be readily tailored to produce a refrigerant fluid capable of meeting the flammability and performance requirements of a particular cooling or heating application.

The compound 1,1,1,2,3,3,3-heptafluoropropane is known in the art and has been shown to be an efficient fire suppression agent. See, e.g., M. Robin, "Large Scale Testing of Halon Alternatives," 1991 International CFC and Halon Conference, Baltimore, MD, December 3-5, 1991; and M. Robin, "Halon Alternatives: Recent Technical Progress," 1992 Halon Alternatives Technical Working Conference, Albuquerque, NM, May 12-14, 1992. Hence, nonflammable mixtures may be obtained upon combination of 1,1,1,2,3,3,3-heptafluoropropane with flammable compounds such as R32, R143a, R143, R152a, R170, R50, R290, R600, dimethyl ether and isobutane.

Of particular advantage are the mixtures of this invention consisting of 1,1,1,2,3,3,3-heptafluoropropane and difluoromethane (R32). Difluoromethane (R32) is known in the art, and has seen some application as a refrigerant. Its uses as a refrigerant are limited, however, due to its flammability and also due to its high vapor pressure. Mixtures of 1,1,1,2,3,3,3-heptafluoropropane and R32 are particularly advantageous as such mixtures can serve as

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drop-in replacements for R22 in heat pump applications, providing a nonflammable refrigerant characterized by discharge pressures low enough to allow use of the mixture in conventional heating and cooling equipment. For example, 5 vapor compression cycle calculations indicate a 30:70 by weight mixture of R32 and 1,1,1,2,3,3,3-heptafluoropropane offers essentially identical energy efficiency as R22, and has a volumetric capacity virtually identical to that of R22. This matching of the volumetric capacities allows the 10 use of the mixture without having to change the compressors currently employed in R22 systems. Mixtures of 1,1,1,2,3,3,3-heptafluoropropane and R32 containing greater than 30 weight percent of R32 are characterized by volumetric capacities greater than that of R22, allowing the use of 15 smaller, less expensive compressors.

Additional mixtures of this invention of particular advantage are those of 1,1,1,2,3,3,3-heptafluoropropane and R152a. These can be readily employed as a replacement for R12 in refrigerator-freezer systems. Such mixtures are 20 capable of providing energy efficiency comparable to or better than that of R12, and have essentially identical volumetric refrigerant capacity.

It is therefore a further feature of the present invention to provide refrigerant mixtures which are 25 efficient, nontoxic, non-ozone depleting and nonflammable, and also which are characterized by operating pressures low enough to allow their use in conventional refrigeration and heating equipment.

The inventive mixtures are useful in both heating and 30 cooling applications. In one process embodiment of the invention, the mixtures of this invention may be used, in the presence of a suitable lubricant if required, in a method for producing refrigeration which comprises condensing the mixtures and thereafter evaporating the mixtures in the 35 vicinity of a body to be cooled. In another process

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embodiment of the invention, the mixtures of the invention may be used, in the presence of a suitable lubricant if required, in a method for producing heat which comprises condensing the mixture in the vicinity of a body to be
5 heated, and thereafter evaporating the mixture.

As described in U.S. Patent No. 4,559,154 to Powell, the usefulness of a material as a heat pump fluid is usually expressed as a coefficient of performance (COP), defined as the ratio of quantity of heat extracted to the amount of work
10 expended. The COP is a universally accepted measure useful in representing the relative thermodynamic efficiency of a refrigerant in a specific cooling or heating cycle. As pointed out by Powell, op. cit., the COP of a fluid may be estimated from the thermophysical properties of the fluid
15 (e.g., vapor pressure curve, molecular weight, vapor and liquid specific heats, etc.). The performance of a refrigerant mixture at specific operating conditions can be derived from the thermodynamic properties of the refrigerant mixture using standard techniques, such as those described
20 for example by R.C. Downing in "Fluorocarbon Refrigerant Handbook," Chapter 3, Prentice-Hall (1988). Specifically, refrigerant performance can be derived from a knowledge of the thermophysical properties of the fluid employing the CYCLE7 or CYCLE11 methods developed by the National Institute
25 of Science and Technology (NIST), or via the techniques described in S. Fisher and J. Sand, "Thermodynamic Calculations for Mixtures of Environmentally Safe Refrigerants Using the Lee-Kesler-Plocker Equation of State," Preprints of the 1990 USNC/IIR Purdue Refrigeration
30 Conference, p. 373.

It should be understood that the present compositions may include additional, non-interfering components, for example lubricants, so as to form new refrigeration mixtures. Any such compositions are considered to be within the scope of
35 the present invention.

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The present invention is more fully illustrated by the following examples, which are to be understood as exemplary only, and non-limiting.

EXAMPLE 1

5 The performance of mixtures of 1,1,1,2,3,3,3-heptafluoropropane and R152a in a typical heat pump application were determined as discussed above, and the results are shown in Table 1. The performance of R22, which is currently employed in such systems, is also shown for
10 reference.

TABLE 1

	Weight R227ea	Percent R152a	COP ¹	Capacity ²	Discharge P (kPa)	Discharge T (°K)
15	0.8	0.2	0.96	0.48	937	320
	0.6	0.4	0.99	0.53	996	322
	0.4	0.6	1.02	0.58	1037	326
	0.2	0.8	1.03	0.61	1067	328
	R22		1.00	1.00	1769	337

20 Condenser inlet: 27.8° C; Condenser outlet: 37.4° C
Evaporator inlet: 26.7° C; Evaporator outlet: 13.8° C
1, 2: Relative to R22

As seen in Table 1, the mixtures of 1,1,1,2,3,3,3-heptafluoropropane and R152a offer several advantages over the presently employed agent R22. Energy
25 efficiency (COP) is slightly higher for the mixtures, and the lower discharge temperatures and pressures result in longer compressor life and more reliable compressor performance.

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EXAMPLE 2

The performance of a 25:75 weight percent mixture of 1,1,1,2,3,3,3-heptafluoropropane and R152a in a typical refrigerator-freezer application was determined employing the method of Example 1, and the results are shown in Table 2. The performance of R12, which is currently employed in such systems, is included in Table 2 for reference.

TABLE 2

Thermodynamic Performance of 25:75 R227ea/R152a Mixture				
Evaporator T = 248° K				
	COP	Capacity	Discharge T (°K)	Discharge P (kPa)
R12	1.00	1.00	324	815
15 R227ea/ R152a	1.06	0.94	327	770
Evaporator T = 256° K				
	COP	Capacity	Discharge T (°K)	Discharge P (kPa)
R12	1.00	1.00	321	819
20 R227ea/ R152a	1.05	0.94	324	775

The data in Table 2 show that the 25:75 blend of R227a and R152a provides essentially the same volumetric capacity as R12 and superior energy efficiency (COP). Lower discharge pressures with the mixture also contribute to longer compressor life and more reliable compressor operation.

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EXAMPLE 3

The performance of a 20:80 weight percent mixture of R227ea and R152a was evaluated in a commercial upright refrigerator-freezer following a procedure similar to that described in ANSI/AHAM HRF-1-1988, "American National Standard: Household Refrigerators/Household Freezers", Section 8, and also described in Vineyard, et al., "CFCs: Time of Transition," ASHRAE, 1989, p. 205. The R12 lubricant was first removed from the unit and replaced with a polyol ester type lubricant, and the system was then charged with 3.0 ounces of the 20:80 mixture of R227ea and R152a. The results are shown in Table 3, which includes the results observed for R12 as a reference.

TABLE 3

	COP	Capacity (Btu/h)	KWh/d
R12	1.29	685	1.85
R227ea/ R152a (20:80)	1.26	623	1.83

As seen in Table 3, the 20:80 mixture of R227ea and R152a consumes less power in operation (lower KWh/d) than the presently employed refrigerant R12. It should be noted that the above test is not performed under optimum conditions, as no attempt was made to change the expansion valve in the refrigeration system. Hence even greater gains in efficiency may be obtainable with the R227ea/R152a mixtures by adjustment of the expansion device.

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EXAMPLE 4

The performance of a 50:50 by weight mixture of R227ea and R152a was evaluated in a commercial upright refrigerator-freezer as described in Example 3, employing a 4.8 ounce charge of the 50:50 mixture. The observed COP was 1.19 and the volumetric capacity was determined to be 590 BTU/h. Power consumption was measured to be 1.92 KWh/day.

EXAMPLE 5

The performance of mixtures of R227ea and R32 were evaluated as described in Example 1, and the results are shown in Table 4.

TABLE 4

	Weight R32	Percent R227ea	COP ¹	Capacity ²	Discharge T (°K)	Discharge P (kPa)
15	0.1	0.9	0.97	0.62	324	1200
	0.2	0.8	1.00	0.80	329	1494
	0.3	0.7	1.01	0.96	333	1742
	0.4	0.6	1.01	1.09	336	1957
	0.5	0.5	1.01	1.22	338	2148
20	0.6	0.4	1.01	1.33	341	2320
	0.7	0.3	1.01	1.42	343	2474
	0.8	0.2	1.01	1.51	345	2609
	0.9	0.1	1.00	1.59	348	2720
	R22		1.00	1.00	337	1769

25 Condenser inlet: 27.8° C; Condenser outlet: 37.4° C
 Evaporator inlet: 26.7° C; Evaporator outlet: 23.8° C
 1, 2: Relative to R22

As the results in Table 4 demonstrate, the mixtures are capable of providing energy efficiency and volumetric

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capacity equal or superior to that of R22. A 30:70 weight percent mixture of R32 and R227ea for example can serve as a drop-in replacement for R22, providing virtually identical efficiency (COP) and volumetric capacity.

5

EXAMPLE 6

The performance of mixtures of R227ea and R290 were evaluated as described in Example 1, and the results are shown in Table 5.

TABLE 5

10	Weight R227ea	Percent R290	COP ¹	Capacity ²	Discharge T (°K)	Discharge P (kPa)
	0.1	0.9	0.92	0.76	320	1560
	0.3	0.7	0.93	0.73	321	1471
	0.5	0.5	0.94	0.68	321	1359
15	0.7	0.3	0.94	0.60	321	1211
	0.9	0.1	0.92	0.48	321	998
	R22		1.00	1.00	337	1769

Condenser inlet: 27.8° C; Condenser outlet: 37.4° C
 Evaporator inlet: 26.7° C; Evaporator outlet: 13.8° C

20 1, 2: Relative to R22

As can be seen from the results in Table 5, the R227ea/R290 mixtures are capable of providing efficiency (COP) close to that of R22, and are also characterized by lower discharge temperatures and pressures compared to R22, leading to longer compressor life and more reliable compressor operation.

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EXAMPLE 7

The performance of a 70:30 by weight mixture of R227ea and dimethyl ether was evaluated in a commercial upright refrigerator-freezer as described in Example 3, employing a 3.6 ounce charge of the 70:30 mixture. The observed COP was 1.14 and the volumetric capacity was 460 BTU/h. Power consumption was measured to be 1.99 KWh/day.

EXAMPLE 8

The performance of a 75:25 by weight mixture of R227ea and isobutane was evaluated in a commercial upright refrigerator-freezer as described in Example 3, employing 3.0 ounce charge of the 75:25 mixture. The observed COP was 0.57 and the volumetric capacity was 228 BTU/h. Power consumption was measured to be 2.83 KWh/d.

EXAMPLE 9

Evaluation of mixtures of R227ea and each of methane (R50), ethane (R170), butane (R600), 1,1,1-trifluoroethane (R143a) and 1,1,2-trifluoroethane (R143) also demonstrates that the resulting compositions provide suitable energy efficiency and volumetric capacity for use in cooling and heating applications. Optimization for these compositions, as well mixtures of R227ea with R32, R152a and R290 as in the foregoing examples, may be made for various applications, and suitable compositions are obtained for various blends ranging from 10 to 90 percent by weight R227ea, particularly from 20 to 80 percent by weight R227ea. The non-R227ea component may also comprise more than one of the other listed compounds. Selection of weight percentages for the respective compounds is made based on flammability and performance requirements of a particular cooling or heating application.

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Example 10

The performance of 30:70 by weight blends of 1,1,1,2,3,3,3-heptafluoropropane (R227ea) with 2-chloro-1,1,1,2-tetrafluoroethane (R124), pentafluoroethane (R125), 1,1,2,2-tetrafluoroethane n(R134), 1,1,1,2-tetrafluoroethane (R134a) and cyclopropane (RC270) was determined employing the method of Example 1, and the results are shown in Table 6.

Table 6

10		COP ¹	Capacity ²	Discharge P (kPa)	Discharge T(°K)
	R227ea(30)/ R124(70)	0.96	0.38	738	320
15	R227ea(30)/ R125(70)	0.89	0.83	1791	323
	R227ea(30)/ R134(70)	0.97	0.50	955	320
	R227(30)/ R134a(70)	0.96	0.58	1125	321
20	R227ea(30)/ RC270(70)	1.02	0.70	1215	330
	R134a	0.97	0.63	1213	324
	R22	1.00	1.00	1769	337

25 Condenser inlet: 27.8°C; Condenser outlet: 37.4°C
Evaporator inlet: 26.7°C; Evaporator outlet: 13.8°C

1,2: Relative to R22

As can be seen from the results in Table 6, the mixtures

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are capable of providing efficiencies (COP) approaching or exceeding that of R22, and are in general characterized by lower discharge pressures and temperatures, leading to more reliable compressor operation and longer compressor life.

- 5 Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

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What is claimed is:

1. In a refrigeration process which utilizes a refrigerant, the improvement comprising using as the refrigerant a composition comprising:

- 5 (a) 1,1,1,2,3,3,3-heptafluoropropane; and
 (b) one or more compounds selected from the group consisting of methane, ethane, propane, butane, difluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,2-trifluoroethane, dimethyl
10 ether, isobutane, 2-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane and cyclopropane.

2. The improvement of claim 1 wherein the concentration of 1,1,1,2,3,3,3-heptafluoropropane in the refrigerant
15 composition is between about 10 and about 90 percent by weight.

3. The improvement of claim 1 wherein the concentration of 1,1,1,2,3,3,3-heptafluoropropane in the refrigerant composition is between about 20 and about 80 percent by
20 weight.

4. The improvement of claim 1 wherein the refrigerant composition consists essentially of 1,1,1,2,3,3,3-heptafluoropropane and propane.

5. The improvement of claim 4 wherein the concentration
25 of 1,1,1,2,3,3,3-heptafluoropropane is between about 10 and about 90 percent by weight.

6. The improvement of claim 1 wherein the refrigerant composition consists essentially of 1,1,1,2,3,3,3-heptafluoropropane and difluoromethane.

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7. The improvement of claim 6 wherein the concentration of 1,1,1,2,3,3,3-heptafluoropropane is between about 10 and about 90 percent by weight.

8. The improvement of claim 1 wherein the refrigerant
5 composition consists essentially of
1,1,1,2,3,3,3-heptafluoropropane and 1,1-difluoroethane.

9. The improvement of claim 8 wherein the concentration of 1,1,1,2,3,3,3-heptafluoropropane is between about 10 and about 90 percent by weight.

10 10. A refrigerant composition which consists essentially
of:

- (a) 1,1,1,2,3,3,3-heptafluoropropane; and
- (b) one or more compounds selected from the group
consisting of methane, ethane, propane, butane,
15 difluoromethane, 1,1-difluoroethane,
1,1,1-trifluoroethane, 1,1,2-trifluoroethane, dimethyl
ether, isobutane, 2-chloro-1,1,1,2-tetrafluoroethane,
pentafluoroethane, 1,1,2,2-tetrafluoroethane,
1,1,1,2-tetrafluoroethane and cyclopropane.

20 11. The composition of claim 10 wherein the
concentration of 1,1,1,2,3,3,3-heptafluoropropane is between
about 10 and about 90 percent by weight.

12. The composition of claim 11 wherein the
concentration of 1,1,1,2,3,3,3-heptafluoropropane in the
25 refrigerant composition is between about 20 and about 80
percent by weight.

13. The composition of claim 10 and which further
includes a lubricant.

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14. A method for producing cooling which comprises
condensing a refrigerant composition and thereafter
evaporating said refrigerant composition in a heat exchange
relationship with a body to be cooled, the refrigerant
5 composition consisting essentially of
1,1,1,2,3,3,3-heptafluoropropane, and one or more compounds
selected from the group consisting of methane, ethane,
propane, butane, difluoromethane, 1,1-difluoroethane,
1,1,1-trifluoroethane, 1,1,2-trifluoroethane, dimethyl ether,
10 isobutane, 2-chloro-1,1,1,2-tetrafluoroethane,
pentafluoroethane, 1,1,2,2-tetrafluoroethane,
1,1,1,2-tetrafluoroethane and cyclopropane.

15. The method of claim 14 wherein the concentration of
1,1,1,2,3,3,3-heptafluoropropane in the refrigerant
15 composition is between about 10 and about 90 percent by
weight.

16. A method for producing heating which comprises
condensing a refrigerant composition in a heat exchange
relationship with a body to be heated and thereafter
20 evaporating the refrigerant composition, the refrigerant
composition consisting essentially of
1,1,1,2,3,3,3-heptafluoropropane, and one or more compounds
selected from the group consisting of methane, ethane,
propane, butane, difluoromethane, 1,1-difluoroethane,
25 1,1,1-trifluoroethane, 1,1,2-trifluoroethane, dimethyl ether,
isobutane, 2-chloro-1,1,1,2-tetrafluoroethane,
pentafluoroethane, 1,1,2,2-tetrafluoroethane,
1,1,1,2-tetrafluoroethane and cyclopropane.

17. The method of claim 16 wherein the concentration of
30 1,1,1,2,3,3,3-heptafluoropropane in the refrigerant
composition is between about 10 and about 90 percent by
weight.

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US93/06043

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : CO9K 5/04

US CL : 252/67; 62/114

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/67; 62/114

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Chemical Abstracts, Dialog heptafluoropropane refig?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>X</u> Y	EP, A, 0,384,371 (Heiskel et al) 29 August 1990. See Abstract and Example III, page 3.	<u>10-12</u> 1-5, 8-17
X	WO, A, 91/16390 (Bivens et al) 31 October 1991. See page 2, line 12- page 3, line 16.	1-3, 8-12, 14-17
<u>X</u> Y	JP, A, 3-93890 (Daikin Kogyo KK) 18 April 1991. See Abstract.	<u>1-3, 6-12</u> 14-17
Y	Chemical Abstracts, Volume 116, Number 22, Abstract 216705v, 1991, "Refrigerant R227", (Preisegger).	13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance		
E earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed	*A*	document member of the same patent family

Date of the actual completion of the international search

26 AUGUST 1993

Date of mailing of the international search report

27 SEP 1993

 Name and mailing address of the ISA/US
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